ON THE INFRARED SPECTRA OF FLUORO-, CHLORO-, BROMO- AND IODOBENZENE IN THE VAPOUR STATE

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ABSTRACT. The infrared spectra of fluorobenzene, chlorobenzene, bromobenzene and iodobenzene in the vapour state have been studied using a Perkin-Elmer one metre gas cell and Model 21 spectrophotometer and compared with the spectra of the pure liquids and of their solutions in carbon tetrachloride and chloroform. Significant changes are observed with the change of state. From the spectra of fluorobenzene and chlorobenzene in the different states it has been concluded that in both these cases the vapour consists of both monomeric and dimeric molecules and the liquid consists almost wholly of dimers. In the other two cases the vapour consists predominantly of monomeric molecules and in the liquid state there is a smaller percentage of monomeric molecules and a greater proportion of dimeric molecules. From a comparison of the spectra with the Raman spectra, some of the bands not assigned by previous workers have been assigned to relevant modes of vibration of the molecules.

INTRODUCTION

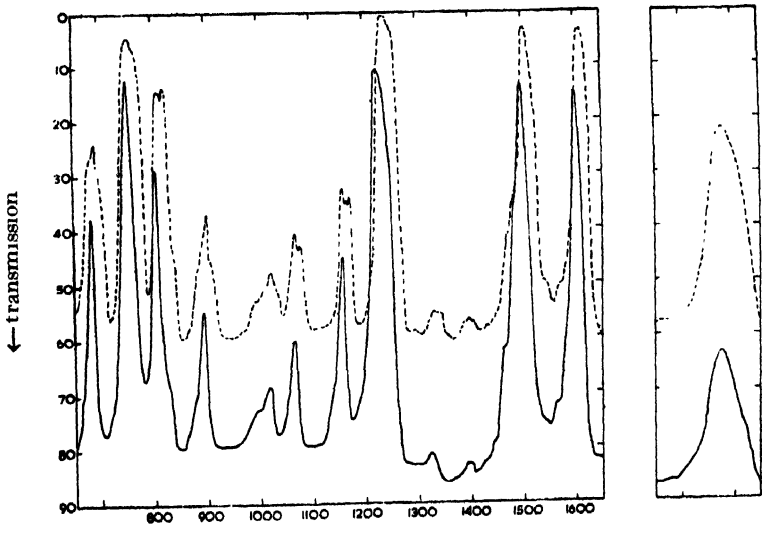
The Raman and infrared spectra of monohalogen substituted benzenes in the state of aggregation and also in solution have been studied by many previous workers (Landolt-Börnstein, 1951; Lecomte, 1937; Mortimer *et al.*, 1947; Plyler, 1949). As the molecules are strongly polar some intermolecular association in the state of aggregation is expected in all these cases. The Raman spectra of chlorobenzene in the vapour and liquid states were studied by Sponer and Kirby-Smith (1941) who observed that in the spectrum due to the vapour some of the lines due to the liquid were shifted and some other lines were absent. Such an effect was also observed by them in the case of three isomeric dichlorobenzenes. As the Raman spectrum of the vapour is generally very weak a definite conclusion regarding the disappearance of some of the lines cannot be drawn. The strength of the infrared absorption in the spectra of the vapour can, however, be increased by increasing the length of the cell. Further, a comparative study of the infrared absorption spectra of the different halogen substituted benzenes in the vapour and liquid states might show whether any significant changes depending on the chemical affinity of the substituent halogen atoms take place with the change from the vapour to the liquid state. With this object in view the infrared spectra of fluorobenzene, chlorobenzene, bromobenzene and iodobenzene in the vapour and liquid states and in solution in different solvents have been studied in the present investigation.

EXPERIMENTAL

The liquids were of chemically pure quality and were distilled under reduced pressure before use. A Perkin-Elmer Model 21 double beam infrared spectrophotometer was used to record the spectra. In the case of the vapours a Perkin-Elmer multiple reflection gas cell with total absorbing path of 100 cm was used. The spectra of the solutions of the compounds in CCl_4, $CHCl_3$ and CS_2 were also recorded using compensation cells in the reference beam. In the case of the pure liquids, thin films enclosed between two NaCl plates were used.

RESULTS AND DISCUSSION

The absorption curves due to the four compounds in the vapour and liquid states are reproduced in Figs. 1, 2, 3 and 4 respectively. The wave numbers in cm^{-1} of the bands are given in Tables I, II, III and IV in which the positions of some of the bands of solutions in different solvents have also been included. The changes observed in the spectra with the change of state and also with dissolution in different solvents are discussed in the following sections.



Frequency in cm^{-1}

Fig. 1. Infrared spectra af fluorobenzene.
..... vapour.
———— liquid.

(a) *Fluorobenzene*

The curves in Fig. 1 show that most of the bands due to the vapour are well resolved while the rest are asymmetric and broad. In the spectrum of the liquid on the other hand, each of the doublets is replaced by a single band. For instance, the liquid gives a strong band 805 cm^{-1} in place of the two bands at 810 and 820 cm^{-1} due to the vapour. In the Raman spectrum of the liquid there is a

TABLE I

Fluorobenzene

ν in cm^{-1}

Liquid	Vapour	3% Soln. in $CHCl_3$	4% Soln. in CCl_4	4% Soln. in CS_2
670 (vw)	675 (w)	665 (w)		670 (w)
		675 (w)		
682 (s)	680 (m, b)	682 (s)	682 (s)	680 (s)
	690 (s)			
	695 (m)			
		710 (m)	728 (s)	
752 (vs)	752 (vs, b)	752 (s)		750 (vs)
	768 (s)			
		795 (vs)		802 (s)
805 (s)	810 (s)		810 (s, b)	
	820 (s)	820 (w)		
825 (w)		840 (vw)		
	885 (w)			850 (w)
895 (m)		895 (m)	892 (m)	890 (m)
	900 (m)			
	908 (w)			
		925 (w)		
998 (vw)	992 (w)			
	1005 (w)	1000 (vw)	1000 (w, b)	1020 (vw)
1020 (w)	1020 (m)	1020 (w)		
1065 (m)	1065 (m)	1065 (m)	1065 (m)	1065 (w)
	1078 (m)			
1155 (s)	1155 (m)	1155 (s)	1157 (s)	1155 (m)
	1170 (m)			
1225 (vs, b)		1215 (vs, b)	1224 (vs)	1222 (vs)
		1225 (vs, b)		
	1238 (vs, b)		1235 (m)	1235 (m)
	1250 (vs)		1250 (vw)	
1326 (vw)	1330 (w)	1325 (w)	1328 (vvw)	
	1340 (w)			
1398 (vw)	1395 (w, b)			
1435 (vw)		1425 (w)	1450 (vvw)	
1465 (w)	1470 (w)	1465 (w)	1465 (w)	
1482 (w)	1485 (w)	1480 (m)	1480 (m)	
1498 (vs)	1502 (vs)	1498 (vs)	1498 (vs)	
	1510 (s)	1515 (vw).		
	1540 (vw)	1530 (vw)		
1565 (vvw)	1570 (vw)			
	1580 (vw)	1585 (vw)	1585 (w)	
	1590 (vw)			
1600 (vs)		1600 (vs)	1600 (vs)	
	1615 (s)			
	1635 (vvw)			
	1695 (vw)			
1700 (vw, b)				
	1708 (w, b)			
	1770 (w, b)			
1850 (vw)	1850 (w)			
	1862 (w)			
	1938 (w)			
1950 (vw)	1952 (m, b)			
2035 (vvw)	2160 (w)			
	2470 (vw)			
	2575 (vvw)			
	2630 (vvw)			
	2890 (vvw)			
		3040 (s)		
3078 (m, b)	3078 (vs, b)		3070 (w, b)	3060 (vw)
	3100 (s)	3100 (w)		

strong line at 806 cm^{-1} which is assigned to the C-F stretching oscillation (Mecke and Kerkhof, 1951). Hence it can be concluded from the observed results that there are two types of molecules in the vapour giving two C–F stretching frequencies and only one of these two types persists in the liquid. Probably, these are the single molecules, and the dimers and the wave number 820 cm^{-1} is to be assigned to the single free molecule and 810 cm^{-1} to the dimer. Again, in place of the two bands 752 cm^{-1} and 768 cm^{-1} given by the vapour only one band at 752 cm^{-1} is given by the liquid. As this band at 752 cm^{-1} is very strong and its frequency is lower than the Raman frequency 759 cm^{-1} given by the liquid, the mode giving the band is different from that giving the Raman line. Probably, the band is due to the mode corresponding to mode No. 18 B of benzene (Pitzer and Scott, 1943) and the band at 752 cm^{-1} is to be assigned to this mode of the dimer.

The strong band at 1502 cm^{-1} given by the vapour has an unresolved companion at 1510 cm^{-1} and there are weak satellites at 1470, 1480 and 1485 cm^{-1} respectively. The spectrum due to the liquid shows a sharp and strong band at 1498 cm^{-1} and two moderately strong satellites at 1465 and 1482 cm^{-1} respectively. This group of bands is due to the mode corresponding to the e_u^- mode No. 19B of benzene. Evidently, the band at 1510 cm^{-1} is due to the single molecule and that at 1502 cm^{-1} to dimers which persist in the vapour. In the liquid the latter frequency diminishes to 1498 cm^{-1} probably owing to formation of hydrogen bonds between neighbouring molecules. The components at 1482 cm^{-1} and 1465 cm^{-1} in the spectrum due to the liquid are stronger than any of the three components given by the vapour. The symmetry of the mode is B_1 in the present case and the two-fold axis in the plane of the molecule passes through the halogen atom. It may be possible, however, that there is small probability of similar alternative sets of displacements taking place with respect to axes passing through diametrically opposite C-H groups in the molecule and the bands at 1485 cm^{-1} and 1470 cm^{-1} may be due to such modes in the single molecules present in the vapour and those at 1480 cm^{-1} and 1565 cm^{-1} might be due to those in the dimer. The slight dependence of the frequency of this mode on the weight of the substituent atom is indicated by the corresponding Raman frequencies of these four halogen substituted compounds. The other component of symmetry A_1 of this mode gives the two bands at 1235 cm^{-1} and 1250 cm^{-1} in the case of the vapour and only a single band at 1225 cm^{-1} in the spectrum due to the liquid, the latter frequency being that of the dimer. The alternative displacements of this mode referred to above would give rise to modes having frequencies near about those of the B_1 mode mentioned above.

It has to be pointed out that the strong band at 1608 cm^{-1} due to the vapour is also accompanied by an unresolved companion at 1615 cm^{-1} and three weak satellites at 1590, 1580 and 1570 cm^{-1} respectively. As this band is due to the B_1 mode corresponding to the e_g^+ mode No. 8B of benzene and the dependence

of the frequency of the vibration on the weight of the substituent atom is very small, the frequency of the dimer is not much different from that of the monomer to show a splitting of the bands 1608 cm^{-1} and 1615 cm^{-1}, the latter being due to the monomer. In this case also, alternative sets of displacements with respect to diametral axes not passing through the halogen atom may occur with a small probability, the satellites 1590 cm^{-1} and 1580 cm^{-1} being the frequencies of such modes in the single molecule. The frequencies of the corresponding modes of the dimer present in the vapour diminish a little in the liquid due probably to intermolecular hydrogen bonding. Other doublets in the region 1000 cm^{-1}—1200 cm^{-1} due to C–H bending oscillations observed in the case of the vapour also appear as single lines in the spectrum due to the liquid. The C—H stretching vibrations of the vapour give bands at 3078 cm^{-1} and 3100 cm^{-1} while in the liquid there is a broad band at 3078 cm^{-1}. This latter band is due to the vibration of the dimer corresponding to mode No. 20B of benzene, the frequency of the monomer being 3100 cm^{-1}.

It can, therefore be concluded from the results that the liquid consists of only dimers and in the vapour there are dimers and monomers almost in equal proportions. The bands observed in the spectra of the solutions in chloroform, carbon tetrachloride and carbon disulphide show that they correspond to the bands given by the pure liquid. In the case of the solution in chloroform the frequency of C–H stretching vibration corresponding to mode 20B is reduced to 3040 cm^{-1}, which shows that hydrogen bonding takes place between the solvent and solute molecules. This band is very weak in the spectra due to solutions in the other two solvents, which shows that in those solutions also the molecules are not free..

(b) *Chlorobenzene*

The spectra due to chlorobenzene in the vapour state and in the liquid state reproduced in Fig. 2 show that the bands at 690, 712, 810, 905 and 1465 cm^{-1} disappear when the vapour is liquefied. The other bands of the vapour of frequencies below 1600 cm^{-1} are broad and asymmetric on the higher frequency side, which suggests that there are unresolved companions on this side. These companions at 750, 1035, 1100, 1250, 1495, 1605 and 3095 cm^{-1} also disappear when the vapour is liquefied. Thus, in this case also it appears that the vapour consists of both associated and single molecules, while the liquid consists wholly of dimers. The frequency of the C–Cl stretching vibration of the single molecule is therefore, 712 cm^{-1} and that of the dimer is 702 cm^{-1} and the latter frequency diminishes to 700 cm^{-1} in the case of the liquid. This shows the formation of intermolecular H...Cl bond in the liquid.

The strong band at 738 cm^{-1} of the liquid may be due to the mode corresponding to mode No. 18B of benzene, the frequency of vibration in the monomer being 750 cm^{-1} represented by an unresolved companion of the band given by the vapour. The bands are broader in the spectrum due to the vapour probably

TABLE II

Chlorobenzene

ν in cm^{-1}

Liquid at 28°C	Vapour at 28°C	3% Soln. in $CHCl_3$	3% Soln. in CCl_4
		665 (w)	
668 (w)			
682 (s)	680 (w)	685 (s)	680 (s)
	690 (m)		
600 (s)	702 (s)	700 (s)	700 (s)
	712 (m)	710 (w)	
			725 (m)
738 (vs)	738 (vs, b)		
	750 (s)		
800 (vvw)	810 (m, b)		
898 (m)	895 (m)	900 (vw)	900 (w)
	905 (w)		
		930 (w)	930 (vw)
1002 (w)	1002 (vw, b)	1000 (vw)	1000 (vw)
1022 (s)	1024 (s)	1025 (s)	1020 (m)
	1035 (m)		
1070 (m)	1070 (w)	1070 (w)	1070 (w)
1082 (s)	1090 (vs)	1085 (vs)	1085 (vs)
	1100 (m)		
1120 (w)	1225 (m)	1120 (w)	1120 (vw)
1155 (vvw)	1150 (vw)		
1170 (vvw)	1170 (vw)		
1235 (m)	1238 (vs)	1225 (vs)	
	1250 (s)		
1430 (vw)	1430 (vvw)	1430 (vw)	
1450 (s)	1450 (w)	1450 (m)	
	1465 (w)		
1480 (vs)	1485 (vs)	1485 (vs)	
	1495 (s)		
1550 (vw)	1550 (vvw)		
1565 (w)	1570 (w)		
1585 (s)	1585 (w)?		
		1590 (m)	
	1598 (vs)		
	1605 (s)		
	1780 (w)		
1860 (vw)			
	1870 (w)		
1950 (vw)	1950 (w)		
	3000 (w)		
3040 (w)		3040 (s)	3035 (vw)
	3050 (w)		
3075 (m, b)	3070 (w)	3075 (w)	
			3080 (w)
	3095 (vs, b)		

because the molecules are free to rotate about the two-fold axis. The band at 1090 cm^{-1} of the vapour is produced by the A_1 component of the mode corresponding to mode No. 19 A of benzene and the B_1 component gives the band at 1485 cm^{-1}. Both the bands are asymmetric on the high frequency side as mentioned earlier, but the latter band is accompanied by weaker satellites

at 1450 and 1465 cm^{-1} respectively. The main band shifts to 1480 cm^{-1}, the band at 1465 cm^{-1} disappears and that at 1450 cm^{-1} becomes stronger when the

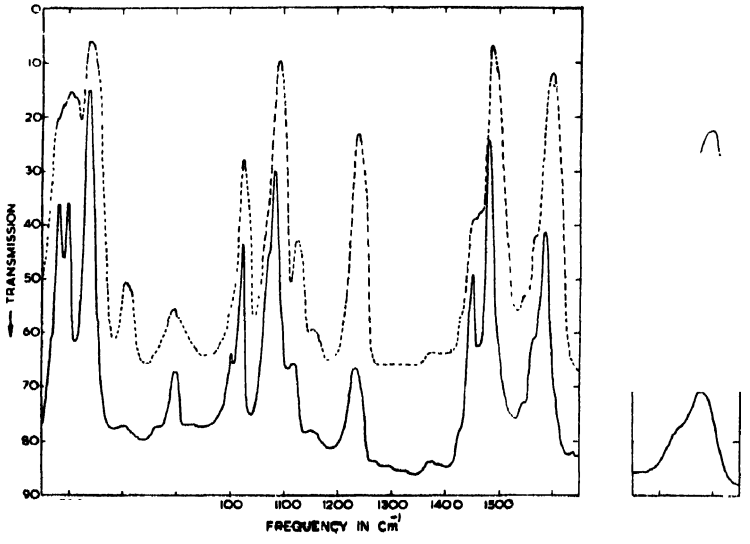


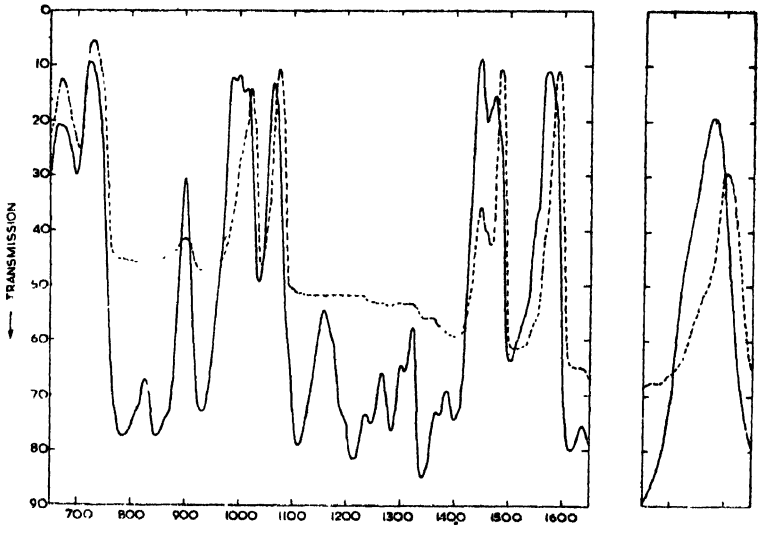
Fig. 2. Infrared spectra of chlorobenzene.
..... vapour.
———— liquid.

vapour is liquefied. As suggested in the case of fluorobenzene these satellites may be due to alternative sets of displacements with respect to the axes passing through diametrically opposite C–H groups of the molecule and the strengthening of the band at 1450 cm^{-1} of the liquid shows that in the dimer such alternative sets of displacements become more probable. The band at 1598 cm^{-1} due to the vapour has similarly weaker companions at 1570 cm^{-1} and 1550 cm^{-1}. The strong band shifts to 1586 cm^{-1} and the other two to 1565 cm^{-1} and 1545 cm^{-1} respectively in the case of the liquid. The corresponding Raman frequency of the molecule in the liquid state is 1584 cm^{-1} and it has been assigned to the A_1 component corresponding to mode No. 8A of benzene by Mecke and Kerkhof (1951). Hence this frequency is to be assigned to the dimer.

The strong bands at 3095 cm^{-1} and the weaker one at 3050 cm^{-1} given by the vapour are due to vibrations corresponding to modes 20B and 7B of benzene respectively. These bands appear to be due to the monomer, the corresponding bands due to the dimer are weak and have frequencies 3070 cm^{-1} and 3040 cm^{-1} respectively. In the spectrum due to the liquid there are a moderately strong band at 3075 cm^{-1} and a weak band at 3038 cm^{-1}. So, it appears that the C—H vibration is partially suppressed in the dimers present in the liquid. In the spectrum due to the 3% solution in chloroform the band at 3040 cm^{-1} is much stronger than that at 3075 cm^{-1}. The former band is thus due to the molecules associated with the chloroform molecules through weak H...Cl bond.

(c) *Bromobenzene*

The bands due to bromobenzene in the vapour and liquid states reproduced in Fig. 3 show remarkable changes in the spectra with the change of state. The strong band at 1483 cm^{-1} due to the vapour has two weak companions at 1460 1448 cm^{-1} respectively. In the spectrum due to the liquid on the other hand, the band at 1447 cm^{-1} is the strongest and there are a weaker companion at 1472 cm^{-1} and another still weaker component at 1485 cm^{-1}. These changes can be explained on the assumption that in the case of the vapour the very strong band at 1483 cm^{-1} is due to the B_1 mode in the single molecule corresponding to mode 19B of benzene and the weak band at 1448 cm^{-1} is due to the same vibration in one of the molecules in the small percentage of dimers present in the vapour. In the liquid the percentage of dimers is larger than that of the monomeric molecule and therefore the band at 1448 cm^{-1} becomes much stronger than that at 1483 cm^{-1}. The intermediate band at 1472 cm^{-1} may be due to the same vibration in the second molecule in the dimer. Similarly, the band at 1590 cm^{-1} due to the vapour has a weak component at 1570 cm^{-1} which becomes very strong in the spectrum due to the liquid, while the component at 1590 cm^{-1} becomes very weak. This latter band is thus due to the single molecule and the band at 1570 cm^{-1} is due to the dimer. The group of bands at 1020 cm^{-1} due to the



Frequency in cm^{-1}

Fig. 3. Infrared spectra of bromobonzene.
..... vapour.
——— liquid.

vapour also undergoes remarkable changes with the change from vapour to the liquid state. In the case of the vapour the strong band at 1022 cm^{-1} has two weak companions at 1010 cm^{-1} and 1000 cm^{-1} respectively. In the spectrum

due to the liquid the band at 1000 cm^{-1} becomes the strongest and there are a strong new band at 990 cm^{-1} and a slightly weaker band at 1015 cm^{-1}. In the Raman spectrum of the liquid there is a strong line at 1000 cm^{-1} due to the breathing vibration of the ring, but this vibration gives a very weak band at the same position in the infrared spectra due to fluoro- and chlorobenzene in the liquid state. The other band at 1022 cm^{-1} is due to the A_1 mode corresponding to mode No. 12 of benzene. The band at 1072 cm^{-1} due to the vapour only shifts to 1065 cm^{-1} without any change in its strength. The Raman line of this frequency-shift is very strong and it has been assigned by previous workers to the A_1 mode corresponding to mode No. 19A of benzene. It appears, however, that the struc- of the band at 1072 cm^{-1} does not change with the change of state, and therefore, this band may be due to the C–H bending vibration. In that case the band at 1010 cm^{-1} may be due to the A_1 component mentioned above in the single molecule and the band at 990 cm^{-1} may be due to the same mode in the dimer. The band at 1000 cm^{-1} is then to be assigned to the breathing vibration of the ring both in the monomeric and dimeric molecules.

The C–H stretching vibrations in the vapour give a very strong band 3105 cm^{-1} and two weak bands at 3075 and 3065 cm^{-1} respectively. In the spectrum due to the liquid the strong band shifts to 3075 cm^{-1} and there is a weak band at 3040 cm^{-1}. The band 3075 cm^{-1} is thus to be assigned to a mode in the dimer corresponding to mode No. 20B of benzene. The corresponding band due to the single molecules in the liquid seems to be extremely weak.

The spectra due to the solutions of bromobenzene in carbon tetrachloride and chloroform are slightly different from the spectrum due to the pure liquid. The band 725 cm^{-1} of the liquid shifts to 718 cm^{-1} and 710 cm^{-1} respectively in the spectra of the two solutions. As this band is also due to a C–H bending oscillation, the shifts mentioned above indicate the formation of weak hydrogen bonds with the chlorine atoms of the solvent molecules. The relative stengths as well as frequencies of the bands 1485 and 1470 cm^{-1} of the liquid also undergo changes when the liquid is dissolved in the two solvents mentioned above. The strong band 1470 cm^{-1} of the liquid shifts to 1465 cm^{-1} and becomes weaker while weaker band 1485 cm^{-1} shifts to 1475 cm^{-1} and becomes very strong in the cases of both the solutions. Such changes are also observed in the cases of the bands 1585 cm^{-1} and 1570 cm^{-1} of the liquid which shift to 1575 and 1565 cm^{-1} respectively in the spectra of both the solutions. Finally, the band 3040 cm^{-1} due to C–H stretching oscillation in the liquid shifts to 3030 cm^{-1} and becomes stronger while the band 3075 cm^{-1} shifts to 3080 and becomes very weak when the liquid is dissolved in chloroform.

(d) *Iodobenzene*

It can be seen from Fig. 4 that although the absorption due to the vapour is weak owing to the low vapour pressure in the cell, the relative strengths of some

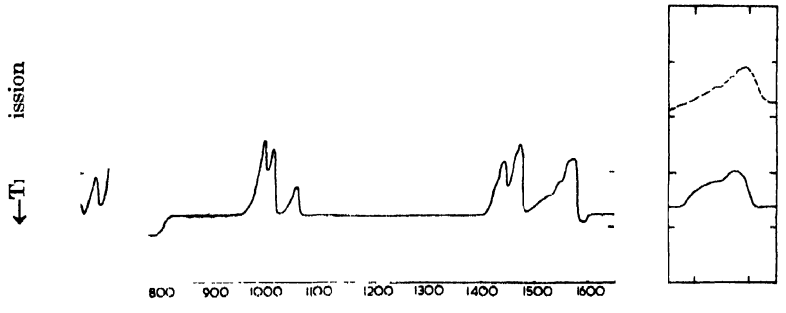
TABLE III

Bromobenzene

ν in cm^{-1}

Liquid at 28°C	Vapour at 28°C	4% Solution in CCl_4	3% Solution in $CHCl_3$
665 (s)			
	670 (m)	670 (vs)	670 (s, vb)
674 (s)			
	678 (m)	680 (m)	
725 (vs, b)	728 (vs, b)	718 (s)	710 (m)
825 (vw)			875 (w)
900 (s)	900 (vw)	900 (w)	900 (vw)
990 (vs)		990 (s)	990 (vw)
1000 (vs)	1000 (m)	1000 (s)	1000 (w)
	1010 (m)		
1016 (s)	1020 (s)	1018 (vs)	1020 (s)
			1045 (m)
1064 (vs)	1072 (vs)	1065 (vs)	1065 (s)
1160 (m)			
1175 (m)			
1175 (m)			
1195 (w)			
1235 (vw)			
1265 (w)			
1300 (vw)			
1322 (m)			
1362 (vw)			
1385 (w)			
			1400 (w)
		1428 (w)	1425 (w)
1447 (vs)	1448 (m)	1448 (vs)	1445 (vs)
1470 (s)	1460 (w)	1465 (w)	1465 (w)
		1475 (vs)	1475 (vs)
1485 (m)	1484 (vs)		
1515 (vw)		1515 (vw)	
1530 (w)		1530 (vw)	
1550 (m)	1550 (vw)	1550 (m)	1550 (vw)
1570 (vs)	1570 (m)	1565 (s)	1565 (s)
		1575 (s)	1578 (vs)
1585 (s)	1588 (vs)		
1638 (w)	1640 (vw)		
1700 (vw)			
1726 (w)			
1775 (vw)	1775 (vw)		
1788 (w)	1788 (w)		
1862 (m)	1850 (vw)	1860 (w)	
	1870 (w)		
1880 (w)	1880 (w)		
1952 (m)	1952 (w)	1948 (w)	
1975 (w)	1970 (w)		
3040 (m)	3060 (w)	3040 (w)	3020 (s, vb)
3075 (vs, b)	3075 (w)	3075 (s)	3080 (vw)
	3102 (vs, b)		

of the bands are different from those of the corresponding bands due to the pure liquid. The very weak band at 1445 cm^{-1} of the vapour becomes strong and the band 1482 cm^{-1} shifts to 1475 cm^{-1} in the spectrum due to the liquid. The band at 1018 cm^{-1} of the vapour is accompanied by weaker bands at 1010, 1000, 986 and 975 cm^{-1} respectively, but in the spectrum due to the liquid the band at 998 cm^{-1} is stronger than the band 1015 cm^{-1} while the band 1010 cm^{-1} is absent. These changes can be explained on the assumptions that in this case also the vapour consists predominantly of monomeric molecules with a small percentage of dimers which increases when the vapour is liquefied and that the line 998 cm^{-1} may be due to the A_1 mode of the single molecule in the liquid corresponding to mode No. 19A of benzene and the band 990 cm^{-1} may be the corresponding band of the dimer. Similarly, the band 1018 cm^{-1} due to the vapour is to be assigned to mode No. 12 of the benzene ring and the corresponding band of the dimer may be identified with the weak band 1010 cm^{-1}. In the spectrum due to the liquid the strengthening of the latter band and slight shift of the former band may be responsible for producing a single strong band at 1013 cm^{-1}. The bands 1475 and 1443 cm^{-1} of the liquid may also be due respectively to the monomeric and dimeric molecules in the liquid. The formation of hydrogen bond in the liquid is indicated by the fact that the strong band 3090 cm^{-1} due to C–H vibration corresponding to mode 20B of benzene shifts ot 3075 cm^{-1} and becomes relatively weak in the spectrum due to the liquid.



Frequency in cm^{-1}

Fig. 4. Infrared spectra of iodobenzene.
..... vapour.
—— —— liquid.

In the case of the solution in carbon tetrachloride the band 1442 cm^{-1} becomes stronger than the band 1472 cm^{-1} and the weak band 1450 cm^{-1} of the vapour becomes quite strong. Also the line due to C–H valence oscillation shifts to 3078 cm^{-1}. In the spectrum due to the solution in chloroform on the other hand the band 3040 cm^{-1} is stronger than the band 3073 cm^{-1} and there is a new band at 2990 cm^{-1}. The diminution of the frequency from 3090 cm^{-1} to 3078 cm^{-1} in the case may be due to the formation of weak H..Cl bond between the solvent and solute molecules.

TABLE IV

Iodobenzene

ν in cm^{-1}

Liquid at 28°C	Vapour at 28°C	Solution in CCl_4	Solution in $CHCl_3$
640 (vw)			
650 (w)	650 (m, b)	652 (m)	650 (s)
670 (vw)		670 (w)	675 (m)
680 (m)	680 (w)	680 (s)	
723 (vs)	725 (s)	720 (vs)	700 (m)
900 (vw)	890 (vw)	890 (vw)	895 (vvw)
	915 (vw)		920 (vvw)
	975 (vw)		
990 (w)	986 (vw)	998 (vs)	997 (vs)
998 (s)			
	1000 (m)		
1013 (s)	1010 (w)		
	1018 (s)	1012 (s)	1012 (vs)
1060 (m)	1062 (m)	1058 (s)	1055 (m)
		1320 (vw)	1300 (vw)
1430 (w)			1425 (w)
1443 (s)	1445 (vvw)	1440 (vs)	1440s(vs)
1465 (m)		1465 (w)	1465 (w)
1475 (s)	1470 (w)	1470 (s)	1470 (s)
	1482 (s)		
1530 (vw)			
1550 (w)	1550 (vvw)	1550 (m)	1545 (w)
1565 (m)	1570 (m)	1565 (s)	1565 (m)
1576 (s)	1585 (s)		1573 (s)
			2990 (w)
3025 (w, b)	3040 (vw)	3040 (vw)	3038 (vs)
3075 (m, b)	3070 (vw)	3080 (vs)	3075 (w)
	3090 (s)		

It can thus be concluded from the results discussed in the previous sections that the frequencies of the modes of vibration of the single molecules of the four monohalogen substituted benzenes can be obtained only from the spectra of the compounds in the vapour state and that these frequencies are

invariably larger than the corresponding frequencies observed in the spectra of the compounds in the liquid state. The results also show that the intermolecular interaction in the liquid state is stronger in the cases of fluorobenzene and chlorobenzene than in the other two cases and this is in conformity with the larger chemical affinity of these two substituent halogen atoms.

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